

# SLIB Chemistry



# How Fast? The Rate of Chemical Change

### **Contents**

- \* Energy Profiles With & Without Catalysts
- \* Rate of Reaction
- \* Measuring Rates of Reaction
- \* Collision Theory
- \* Factors Affecting Rates of Reaction
- \* Activation Energy
- \* Maxwell-Boltzmann Distribution Curves



# **Energy Profiles With & Without Catalysts**

# Your notes

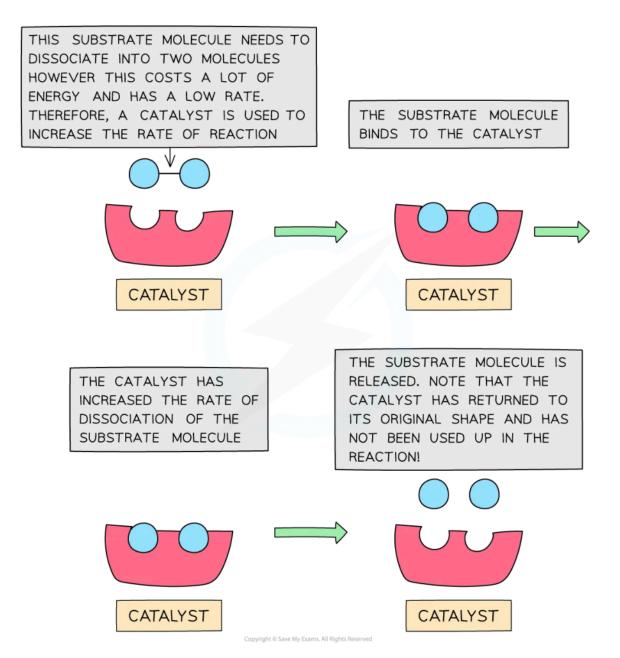
# **Energy Profiles With & Without Catalysts**

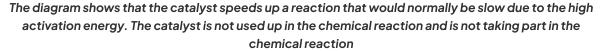
How do catalysts increase the rate of reaction?

- A catalyst increases the rate of a reaction by providing the reactants with an alternative reaction
   pathway which is lower in activation energy than the uncatalysed reaction
- The catalyst remains **chemically unaltered** by the end of the reaction

How a catalyst increases the rate of reaction







- Catalysts are important in reducing the **environmental impact** of industrial processes by:
  - Reducing the energy requirements of processes as they enable reactions to occur at lower temperatures and pressures





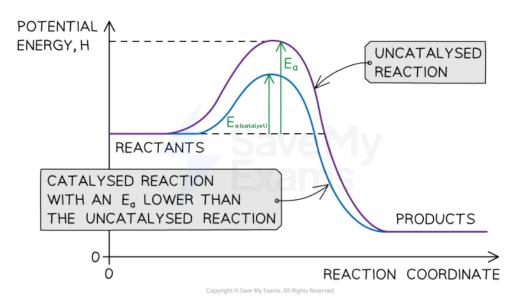
- Reducing waste products as they can be reused and are only used in small quantities, increasing atom economy
- Increasing the selectivity of processes, promoting specific reactions and suppressing undesired
- Your notes

- Catalysts can be divided into two types:
  - Homogeneous catalysts
  - Heterogeneous catalysts
- Homogeneous means that the catalyst is in the same phase as the reactants
  - For example, the reactants and the catalysts are all liquids
- Heterogeneous means that the catalyst is in a different phase to the reactants
  - For example, the reactants are gases but the catalyst used is a solid

### Energy profiles of reactions with catalysts

The lower activation energy of the alternative pathway used by a catalyst can be shown on an energy profile

### Energy profile with and without a catalyst



The diagram shows that the catalyst allows the reaction to take place through a different mechanism, which has a lower activation energy than the original reaction

### **Examples of catalysts**

- Enzymes are biological catalysts
  - Enzymes act as catalysts in biological systems, controlling many biochemical reactions within cells



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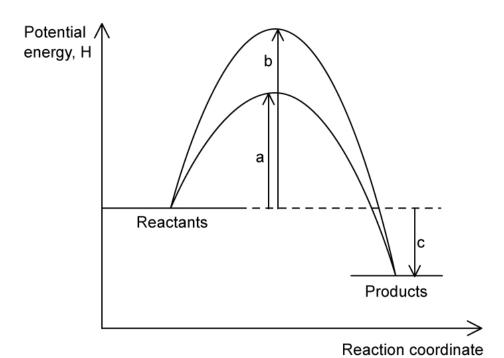
- As well as being important for controlling reactions in cells, they are also important in **industry**
- Enzymes allow industrial reactions to happen at **lower temperatures and pressures** than usually needed, saving money and energy
- Transition metals are often used as catalysts due to their ability to form more than one stable oxidation state
- For more information about the uses of transition metals as catalysts required in Higher Level Chemistry, see our revision note on the Characteristic Properties of Transition Elements



## Worked example

The energy profile below shows the energy changes for a reaction with and without a catalyst.





Which symbols represent the enthalpy change,  $\Delta H$ , and the activation energy,  $E_a$ , for the reaction using a catalyst?

	ΔΗ	$E_a$ (with catalyst)
Α.	а	С
В.	Ь	С
C.	С	а
D.	b - a	С

### Answer:

■ The correct option is **C**.



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- By definition, the enthalpy change is the difference in energy content between reactants and products, in this case, arrow **c**
- The catalyst lowers the activation energy, which corresponds to arrow **a**



### **Rate of Reaction**

# Your notes

### Rate of Reaction

### What is rate of reaction?

- Some reactions take place instantly, but most are much slower and it is possible to measure how long these reactions take to reach a certain stage
- As a chemical reaction proceeds, the concentration of the reactants decreases and the concentration of the products increases
  - Reversible reactions are an exception to this, where the concentration of reactants and products remains constant once dynamic equilibrium has been achieved
- The **rate of a reaction** is the speed at which a chemical reaction takes place and can be expressed as the change in concentration of a particular reactant or product per unit time
- The rate of reaction typically has the units **mol dm**<sup>-3</sup> **s**<sup>-1</sup>

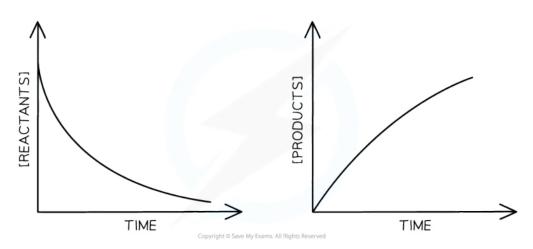
### How to calculate rate of reaction

The rate of reaction formula is:

rate of reaction (mol dm<sup>-3</sup> s<sup>-1</sup>) = 
$$\frac{\text{change in concentration of reactants or products (mol dm}^{-3})}{\text{time (s)}}$$

• Experimental data from reactions can be shown graphically and used to calculate the rate of reaction

### Rate of reaction graphs



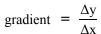
# As the reaction proceeds, the concentration of reactants and products change with time

- The steeper the gradient, the quicker the rate of reaction
- The rate of reaction at a particular time can be found by calculating the gradient of the curve at that time



■ To find the gradient of a curve, draw the tangent to the curve and calculate the gradient of the tangent by using the equation:





# Examiner Tip

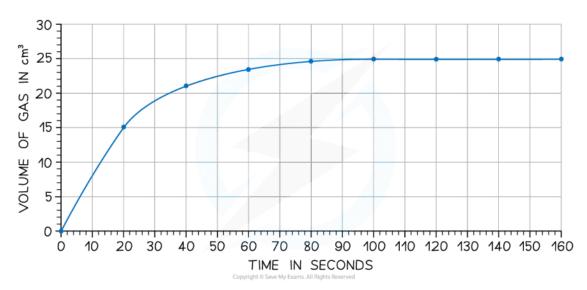
- The rate of reaction is a positive value
- The graph of the reactants' concentration over time shows a negative gradient
  - So, the sign of the rate should be altered to be a positive value
  - E.g. gradient =  $-20.6 \text{ mol dm}^{-3} \text{ s}^{-1} \rightarrow \text{rate} = 20.6 \text{ mol dm}^{-3} \text{ s}^{-1}$
- The graph of the products' concentration over time shows a positive gradient
  - So, the sign of the rate will already be a positive value and not need altering

### Worked example

lodine and methanoic acid react in aqueous solution.

$$I_2(aq) + HCOOH(aq) \rightarrow 2I^-(aq) + 2H^+(aq) + CO_2(g)$$

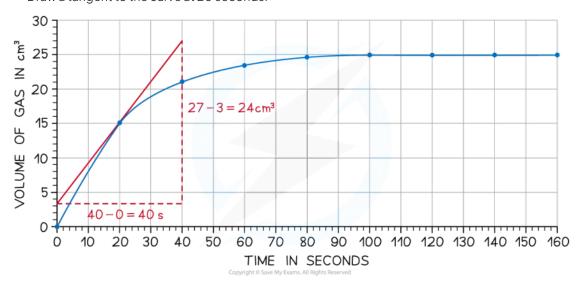
The rate of reaction can be found by measuring the volume of carbon dioxide produced per unit time and plotting a graph as shown:



Calculate the rate of reaction at 20 seconds.

### Answer:

• Draw a tangent to the curve at 20 seconds:







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- Complete the triangle and read off the values of x and y
- Determine the gradient of the line using  $\Delta y / \Delta x$
- Rate of reaction =  $24 \div 40 = 0.60 \text{ cm}^3 \text{ s}^{-1}$



## Examiner Tip

- When drawing the tangent to a curve, you should:
  - Make the triangle large
  - Try to intersect with gridlines if you can
- These points should minimise errors of precision and reduce the chance you will accidentally misread the graph values



# **Measuring Rates of Reaction**

# Your notes

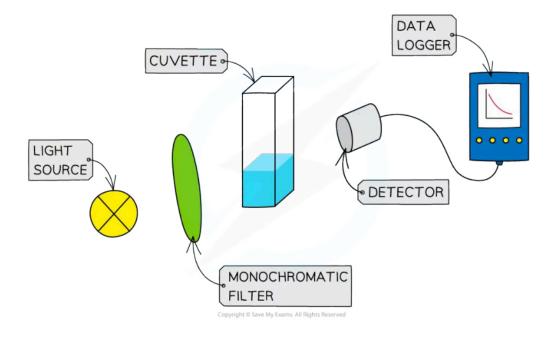
### **Measuring Rates of Reaction**

### Measuring rate of reaction

- To measure the **rate of a reaction**, we need to be able to measure either how quickly the reactants are used up or how quickly the products are formed
- The method used for measuring depends on the substances involved
- There are a number of ways to measure a reaction rate in the lab; they all depend on some property that changes during the course of the reaction
- That property is taken to be **proportional** to the concentration of the reactant or product, e.g., colour, mass, volume
- Some reaction rates can be measured as the reaction proceeds (this generates more data);
  - Faster reactions can be easier to measure when the reaction is over, by averaging a collected measurement over the course of the reaction
- Three commonly used techniques are:
  - Mass loss
  - Gas production
  - Colorimetry

### Measuring the rate of reaction using colorimetry

A colorimeter or spectrophotometer measures the amount of light that passes through a solution
 Colorimetry Set Up



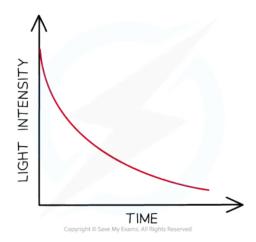


### Colorimetry measures the light intensity of light passing through a sample

- If a solution changes colour during a reaction, this can be used to measure the rate
- The intensity of light reaching the detector is measured every few seconds and the data is plotted to show how the concentration of the reactants or products changes with time
- The light intensity is related to the concentration, so the graph represents a graph of concentration of products or reactants against time

# Your notes

### Examples results from a colorimeter



#### Sketch graph of colour intensity against time (the coloured species is a reactant in this case)

• **Note:** Colorimetry cannot be used to monitor the formation of coloured precipitates as the light will be scattered or blocked by the precipitate

# Examiner Tip

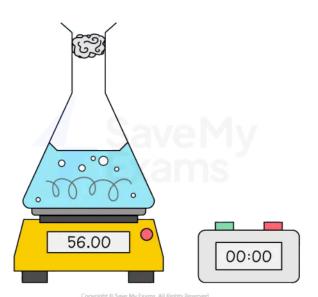
 A colorimeter / spectrophotometer can also measure how much light is absorbed by the sample and the corresponding results show a plot of absorbance against time.

### Measuring the rate of reaction using changes in mass

- When a gas is produced in a reaction it usually escapes from the reaction vessel, so the mass of the vessel decreases
  - This can be used to measure the rate of reaction
  - For example, the reaction of calcium carbonate with hydrochloric acid produces CO<sub>2</sub>
  - The mass is measured every few seconds and the change in mass over time is plotted as the CO<sub>2</sub> escapes

### Equipment used to measure the loss of mass



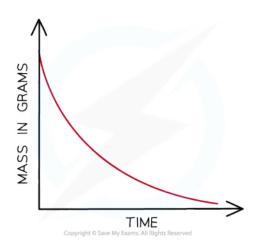




Measuring changes in mass using a balance. The cotton wool in the neck of the flask allows the gas to escape whilst preventing the other reactants and products from leaving the container

• The mass loss provides a measure of the amount of reactant, so the graph is the same as a graph of amount of reactant against time

### A graph to show the change in mass with time



Mass loss of a product against time

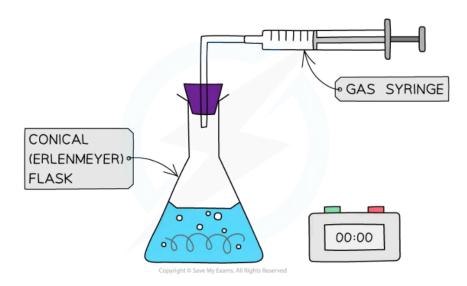
- However, one limitation of this method is the gas must be sufficiently dense or the change in mass is too small to measure on a 2 or 3 decimal place balance
  - So, carbon dioxide would be suitable  $(M_r = 44)$  but hydrogen would not  $(M_r = 2)$

### Measuring rate using changes in volume of gases



- When a gas is produced in a reaction, it can be trapped and its volume measured over time
  - This can be used to measure the rate of reaction.
  - For example, the reaction of magnesium with hydrochloric acid produces hydrogen

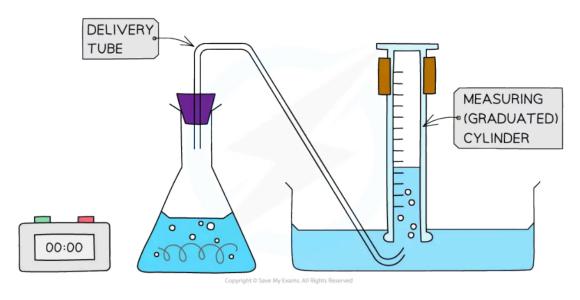
### Measuring rate of reaction using a gas syringe



### Collecting gases experimental set up

- An alternative gas collection set up involves collecting a gas through water by displacement using an inverted measuring cylinder or burette
- This method can only be used if the gas produced has a low water solubility
- Hydrogen gas can be collected using this method

### Measuring the rate of reaction using an inverted measuring cylinder





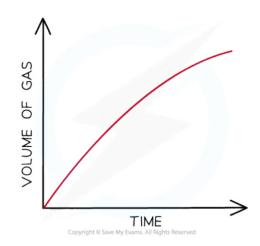




### Alternative gas collection set up

- The volume can be measured every few seconds and plotted to show how the volume of gas varies with time
- The volume provides a measure of the amount of product, so the graph is a graph of the amount of product against time

# Graph of gas volume evolved against time



The volume of gas increases with time. The reaction has stopped when the volume of gas plateaus

### Measuring concentration changes using titrations

- The concentration of a sample can be measured by performing a titration
- However, the act of taking a sample and analysing it by titration can affect the rate of reaction and it cannot be done continuously
- To overcome this, samples of the reaction mixture are taken at regular intervals during the course of the reaction
- The reaction in each of the samples is deliberately stopped this is called quenching
  - Quenching 'freezes' the reaction at a specific point in time to allow the concentration to be determined by titration
- Based on the collected data, the rate of reaction can be calculated by determining the change in concentration with time

### Measuring the rate of reaction using conductivity

- **Conductivity** can be used to measure the rate of a reaction by monitoring changes in the electrical conductivity of the reaction mixture over time
- As the reaction proceeds, the concentration of **ions** in the solution may change, affecting its conductivity
- By measuring the conductivity at different time intervals, the rate of the reaction can be determined based on how quickly the conductivity changes
- For example, in the reaction:





### $HCI(aq) + NaOH(aq) \rightarrow NaCI(aq) + H<sub>2</sub>O(I)$

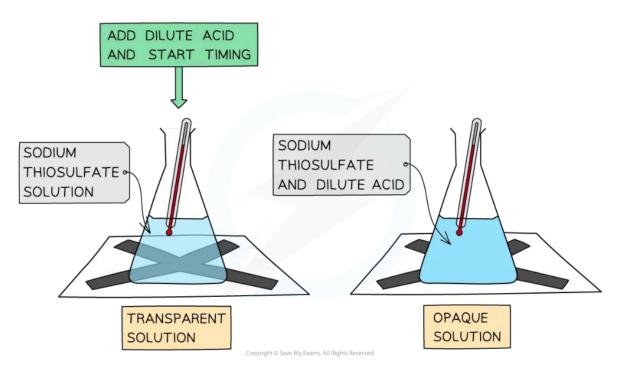
- During this reaction, HCl and NaOH dissociate into ions, increasing the conductivity of the solution
- As the reaction progresses, the concentration of ions changes which affects the conductivity

### Measuring the rate of reaction using a 'clock reaction'

- Often it is more convenient to 'stop the clock' when a specific (visible) point in the reaction is reached instead of continuously monitoring the change in rate
- 'Clock reactions' are non-continuous methods in which the time taken to reach a fixed point is measured
  - For example, when a piece of magnesium dissolves completely in hydrochloric acid
  - Another common rate experiment is the reaction between sodium thiosulfate and hydrochloric acid which slowly produces a yellow precipitate of sulfur that obscures a cross when viewed through the solution:

$$Na_2S_2O_3(aq) + 2HCI(aq) \rightarrow 2NaCIaq) + SO_2(g) + H_2O(I) + S(s)$$

### The reaction of sodium thiosulfate and hydrochloric acid



### The disappearing cross experiment

• The main limitation here is that often it only generates one piece of data for analysis





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# Examiner Tip

- You should be familiar with the interpretation of graphs of changes in concentration, volume or mass against time and be able to calculate a rate from a tangent to the graph
  - For information about drawing tangents on graphs, see our revision note on Graphing in Chemistry





# **Collision Theory**

# Your notes

### **Collision Theory**

### Kinetic energy and temperature

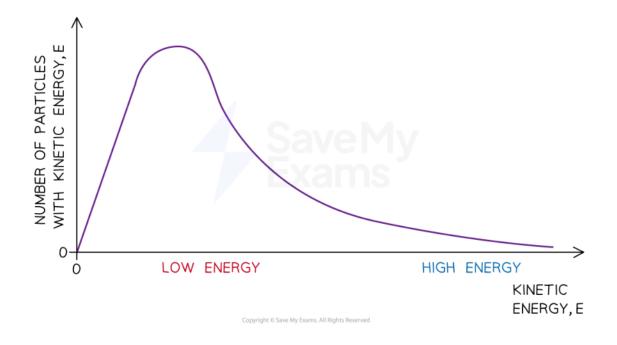
- The **kinetic theory** developed in the 18<sup>th</sup> century out of a need to explain how it is that gases exert pressure inside a container
- Theories about gas particles and movement were extended to include all states of matter
- The **kinetic theory** of matter accounts for the properties of solids, liquids and gases in terms of the interactions of particles and their relative energies

For more information on kinetic theory, see our revision note on The Kinetic Molecular Theory

• **Kinetic energy** refers to the energy associated with movement or motion. It is determined by the mass, *m*, and velocity, *v*, of the substance according to the kinetic energy formula:

$$KE = \frac{1}{2}mv^2$$

- As the **kinetic energy** of the particles at the same temperature is equal, this means there is an inverse relationship between mass and velocity
  - This is why substances with a lower mass diffuse more quickly than those with greater mass at the same temperature
- Particles in a substance have a range of kinetic energies due to their random motion
- The distribution of kinetic energy is shown in the Maxwell-Boltzmann energy distribution curve
   Maxwell-Boltzmann distribution curve





# The Maxwell-Boltzmann energy distribution curve shows the distribution of kinetic energy of particles in a sample



- The area under the curve gives the total number of particles
- The average kinetic energy of the particles is directly proportional to the temperature of the system
  in Kelvin

### What is collision theory?

- Collision theory explains how chemical reactions occur
- When reactants come together the kinetic energy they possess means their particles will collide and some of these collisions will result in chemical bonds being broken and some new bonds being formed
- The rate of a chemical reaction depends on how often a reaction from a collision occurs, this is influenced by the following four factors:
  - Collision frequency
  - Collision energy
  - Activation energy
  - Collision geometry

### Collision frequency

- If a chemical reaction is to take place between two particles, they must first collide
- The number of collisions between particles per unit time in a system is known as the collision
   frequency
- The **collision frequency** of a given system can be altered by:
  - Changing the concentration of the reactants
  - Changing the total pressure
  - Changing the temperature
  - Changing the surface area of the reacting particles

### Collision energy

- Not all collisions result in a chemical reaction
  - Most collisions just result in the colliding particles bouncing off each other
  - Collisions which do not result in a reaction are known as unsuccessful collisions
- Unsuccessful collisions happen when the colliding species do not have enough energy to break the necessary bonds
- If they do not have sufficient energy, the collision will not result in a chemical reaction
- If they have sufficient energy, they will react, and the collision will be **successful** 
  - The combined energy of the colliding particles is known as the collision energy

### Collision energy







#### Collision energy is the combined energy of two colliding particles

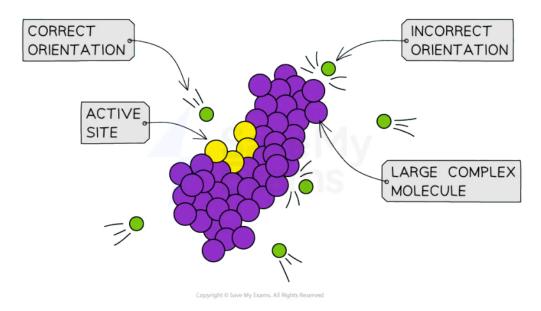
### **Activation Energy**

- The minimum energy the colliding particles need in order to react is known as the **activation energy**
- If the **collision energy** of the colliding particles is less than the activation energy, the collision will be unsuccessful
- If the **collision energy** is equal to or greater than the activation energy, the collision will be successful, and a reaction will take place
- The activation energy can be changed by the addition of a catalyst

### **Collision Geometry**

- Particles have to have the right **orientation** when they collide for the reaction to be **successful** 
  - This is particularly the case with large molecules with complex shapes

### **Collision geometry**



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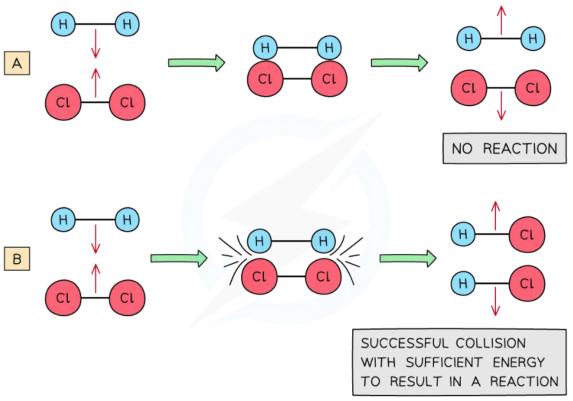


Orientation becomes increasingly important in large complex biomolecules such as proteins and carbohydrates where active sites (reactive part of the molecule) can only be accessed in one orientation



- Most collisions do not result in a reaction because <u>they do not reach the activation energy</u> rather than not having the correct collision geometry
- Ultimately, the rate of reaction depends on the number of successful collisions that happen per unit time
  - A **successful collision** is where the particles collide in the correct orientation **and** with sufficient energy for a chemical reaction to occur
- An unsuccessful collision is when particles collide in the wrong orientation or when they don't have enough energy and bounce off each other without causing a chemical reaction

### Successful and unsuccessful collisions



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Diagram (A) shows an ineffective collision due to the particles not having enough energy whereas (B) shows an effective collision where the particles have the correct orientation and enough energy for a chemical reaction to take place



# **Factors Affecting Rates of Reaction**

# Your notes

### **Factors Affecting Rates of Reaction**

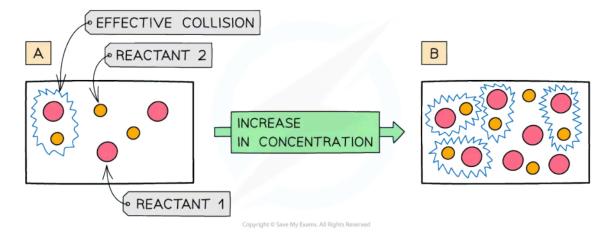
### What are the factors affecting rate of reaction?

- The rate of reaction is dependent on any factor that changes the number of successful collisions
- Five such factors are:
  - Concentration
  - Pressure
  - Temperature
  - Surface area
  - The use of catalysts

### Concentration

- The more **concentrated** a solution is, the **greater** the number of **particles** in a given volume of solvent
- An increase in concentration causes an increased collision frequency and therefore the frequency of successful collisions increases
- This leads to an increased rate of reaction

#### Effect of concentration on rate of reaction



The diagram shows a higher concentration of particles in (b) which means that there are more particles present in the same volume than (a) so the chances and frequency of collisions between reacting particles are increased causing an increased rate of reaction

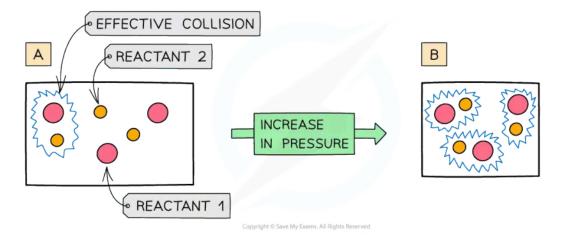
### Pressure

- An increase in pressure in reactions that involve gases has the same effect as an increased concentration of solutions
- When the **pressure** is increased, the particles have less space in which they can move
- This means that the number of successful collisions increases due to an increased collision frequency



• An increase in pressure, therefore, increases the **rate of reaction** 

### Effect of pressure on rate of reaction

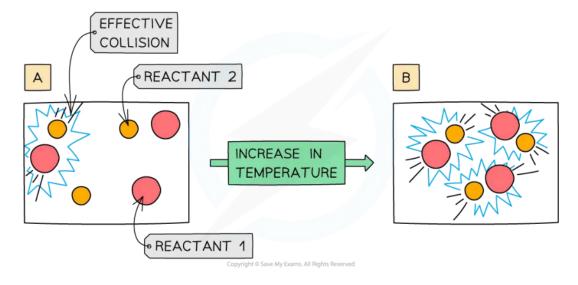


The diagram shows a higher pressure in (b) which means that the same number of particles occupy a smaller volume, resulting in an increased collision frequency and therefore increased rate of reaction

### **Temperature**

- Increasing the temperature of the reaction mixture increases the rate of reaction in the following two ways:
  - At higher temperatures, the particles are moving faster, so collide more frequently
    - A higher number of collisions in total mean a higher **number** of **successful** collisions
  - At higher temperatures, a higher proportion of the particles have the activation energy or more
    - This means that a higher **proportion** of collisions are **successful**

### Effect of temperature on rate of reaction



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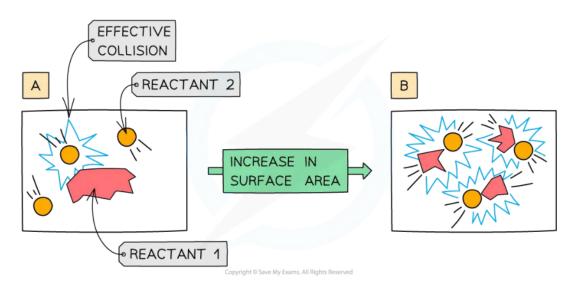
# An increase in temperature causes an increase in the kinetic energy of the particles. The number of collisions increases and the proportion of successful collisions increases

• For more information about how to explain the effect of temperature on the rate of reaction, see our revision note on Maxwell–Boltzmann Distribution Curves

#### Surface area

- Only the particles on the surface of a solid will collide with particles of the other reactant
- If the surface area is increased, more particles will be on the surface and able to collide with particles of the other reactant
  - This means that there will be more collisions in total and therefore more **successful** collisions.
- Surface area can be increased by decreasing the size of the reactant, e.g. from large pieces to a fine powder
  - Large pieces have a much smaller surface area than powders, which have a very large **surface area**

#### Effect of surface area on rate of reaction



# An increase in surface area of a solid reactant allows more particles to come into contact with each other

### Catalysts

- A catalyst provides the reactants with an alternative reaction pathway which is lower in activation energy than the uncatalysed reaction
  - This means that more **collisions** will be **successful**
  - The rate of reaction therefore increases
- A catalyst does not itself undergo permanent chemical change i.e. it is chemically unchanged at the end of the reaction
- For more information on catalysts, see our revision notes on Energy Profiles With & Without Catalysts





## Worked example

Which of the following factors can result in the rate of a chemical reaction increasing?

- I. Increasing the total pressure in reactions involving gases
- II. Raising the temperature in reactions involving gases
- III. Increasing the particle size of a solid in a reaction
- A. land II only
- B. I and III only
- C. II and III only
- **D**. I, II and III

#### Answer:

The correct option is **A**.

- Increasing pressure and raising temperature increases the number of successful collisions
- Increasing the particle size decreases the surface area and reduces the number of collisions





# **Activation Energy**

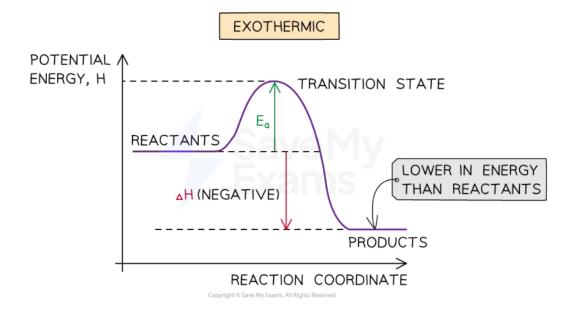
# Your notes

### **Activation Energy**

### What is activation energy?

- For a reaction to take place, the reactant particles need to overcome a minimum amount of energy
  - This energy is called the **activation energy** (E<sub>a</sub>)
- In **exothermic reactions**, the reactants are higher in energy than the products
- In **endothermic reactions**, the reactants are lower in energy than the products

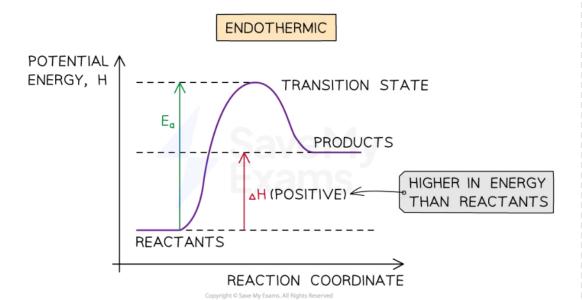
Energy profile of an exothermic reaction, showing Ea



The diagram shows that the reactants are higher in energy than the products in the exothermic reaction

Energy profile of an endothermic reaction, showing Ea





Your notes

### The diagram shows that the reactants are lower in energy than the products in the endothermic reaction

- Even though particles collide with each other in the same orientation, if they don't possess a minimum energy that corresponds to the  $E_a$  of that reaction, the reaction will **not** take place
- Therefore, for a collision to be **successful** the reactant particles must collide in the correct orientation **AND** possess a minimum energy equal to the  $E_a$  of that reaction

# Examiner Tip

### How to find the activation energy of a reverse reaction

• You may be required to show or calculate the activation energy for a reverse reaction using a labelled energy profile like those above. The activation energy for the reverse reaction is found by: For an exothermic reaction =  $\Delta H + E_a$  (forward)

For an endothermic reaction =  $E_a$  (forward) -  $\Delta H$ 

- Calculations of the value of the activation energy from experimental data are not required at Standard Level but are required in Higher Level Chemistry
- For more information on how to calculate activation energy, see our revision notes on Determining Activation Energy & the Arrhenius Factor



### **Maxwell-Boltzmann Distribution Curves**

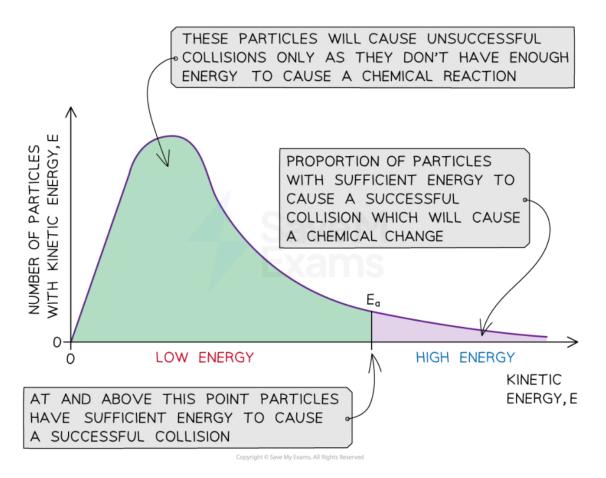
# Your notes

### Maxwell-Boltzmann Distribution Curves

### What is a Maxwell-Boltzmann distribution curve?

- A Maxwell-Boltzmann distribution curve is a graph that shows the distribution of energies at a certain temperature
- In a sample of a substance:
  - A few particles will have very low energy
  - A few particles will have very high energy
  - Many particles will have energy in between

#### Maxwell-Boltzmann distribution curve



The Maxwell-Boltzmann distribution curve shows the distribution of energies and the activation energy

• The graph shows that only a small proportion of particles in the sample have enough energy for an **effective or successful collision** and for a **chemical reaction** to take place

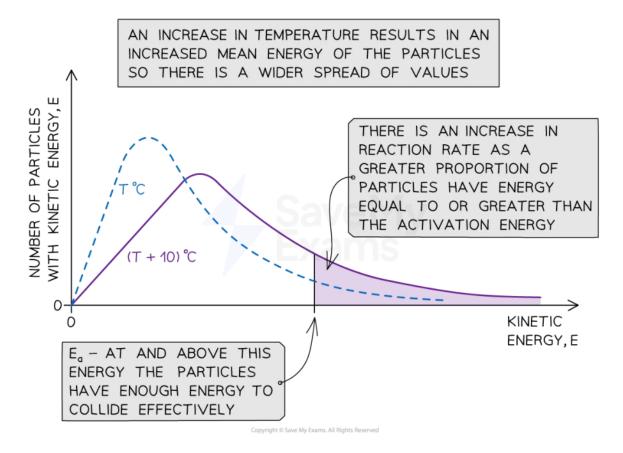


- The most probable energy of a particle is represented by the highest point on the curve's peak
  - This is sometimes written as  $E_{MP}$

# Effect of changes in temperature on the Maxwell-Boltzmann distribution curve

- When the temperature of a reaction mixture is increased, the particles gain more kinetic energy
- This causes the particles to move around faster, resulting in more frequent collisions
- Furthermore, the proportion of **successful collisions** increases, meaning a higher **proportion** of the particles possess the minimum amount of energy (activation energy) to cause a chemical reaction
- With higher temperatures, the Maxwell-Boltzmann distribution curve **flattens** and the peak **shifts** to the right

### Graph of the effect of temperature on the Maxwell-Boltzmann distribution curve



The Maxwell-Boltzmann distribution curve at T°C and when the temperature is increased by 10°C

- Therefore, an increase in temperature causes an increased rate of reaction due to:
  - There being more effective collisions as the particles have more kinetic energy, making them move around faster
  - A greater proportion of the molecules having kinetic energy greater than the activation energy





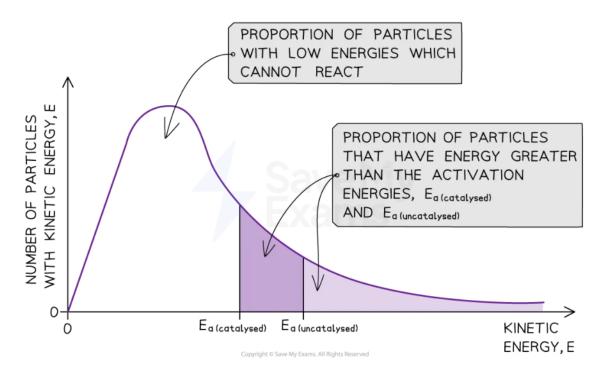
# Examiner Tip

- When drawing Maxwell-Boltzmann distribution curves at different temperatures, make sure that:
  - The peak of the curve of the **higher** temperature is **lower** and to the **right** of the peak of the curve of the lower temperature
  - The two curves should only cross each other once
  - The tail of the curve of the higher temperature should be **higher** than that of the lower temperature
- **Careful:** Examiners currently prefer to ask about the effect of reducing the temperature of a reaction, rather than increasing the temperature
  - The underlying theory is still the same but you need to apply it in the opposite direction

### Effect of a catalyst on the Maxwell-Boltzmann distribution curve

- A catalyst provides the reactants with another reaction pathway which has a lower activation energy
- By lowering E<sub>a</sub>, a greater proportion of molecules in the reaction mixture will have sufficient energy for a successful collision
- As a result of this, the rate of the catalysed reaction is increased compared to the uncatalysed reaction

### Maxwell-Boltzmann distribution curve with a catalyst



The total shaded area (both dark and light shading) under the curve shows the number of particles with energy greater than the  $E_a$  when a catalyst is present. This area is much larger than the dark shaded area





which shows the number of particles with energy greater than the  $E_a$  without a catalyst. The light-shaded area shows the extra particles which have enough energy to react with a catalyst.



### Examiner Tip

- Make sure you know how to sketch and label the axes in Maxwell-Boltzmann distribution curves
  - The curve must start at the origin and it approaches, but **never** touches the x-axis.
- If you are asked to show the area that represents the particles with an energy greater than the activation energy with a catalyst, make sure you highlight the **total** shaded area, not just the light-shaded area.